GREEN CHEMISTRY

What is Green Chemistry?

- Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacturing and application of chemical products to human health and the environment.

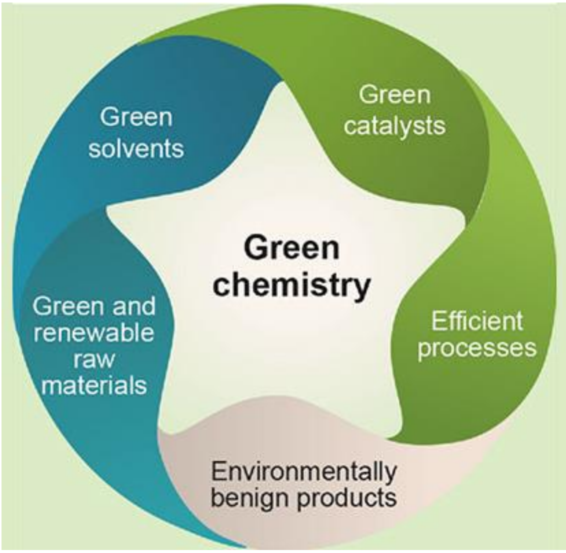
*-by **Paul T. Anastas** & **John C. Warner** (Green chemistry, Theory and Practice, Oxford University Press, New York, **1988**)*

Paul T. Anastas: Father of Green Chemistry

- Green chemistry means preventing pollution before it happens rather than cleaning up the mess later, saving money by using less energy and fewer/safer chemicals, thus reducing the costs of pollution control, waste disposal and space and eliminating the hazard rather than just preventing exposure.
- Green chemistry is pro-active, innovative science which targets pollution prevention at the source, stopping or reducing waste before it even begins.
- Green chemistry, also called **sustainable chemistry**, is a philosophy of chemical research and engineering focused on the designing of products and processes that minimize or eliminates the use and generation of hazardous substances.

Whereas **environmental chemistry** focuses on the effects of polluting chemicals on nature, **green chemistry** focuses on technological approaches to prevent pollution and reducing consumption of nonrenewable resources.

Green Chemistry is about:



- Waste minimization at source
- Use of catalysts in place of reagents
- Using non-toxic reagents
- Use of renewable resources
- Improved atom efficiency
- Use of solvent free or recyclable environmentally benign solvent systems

Goals of Green Chemistry:

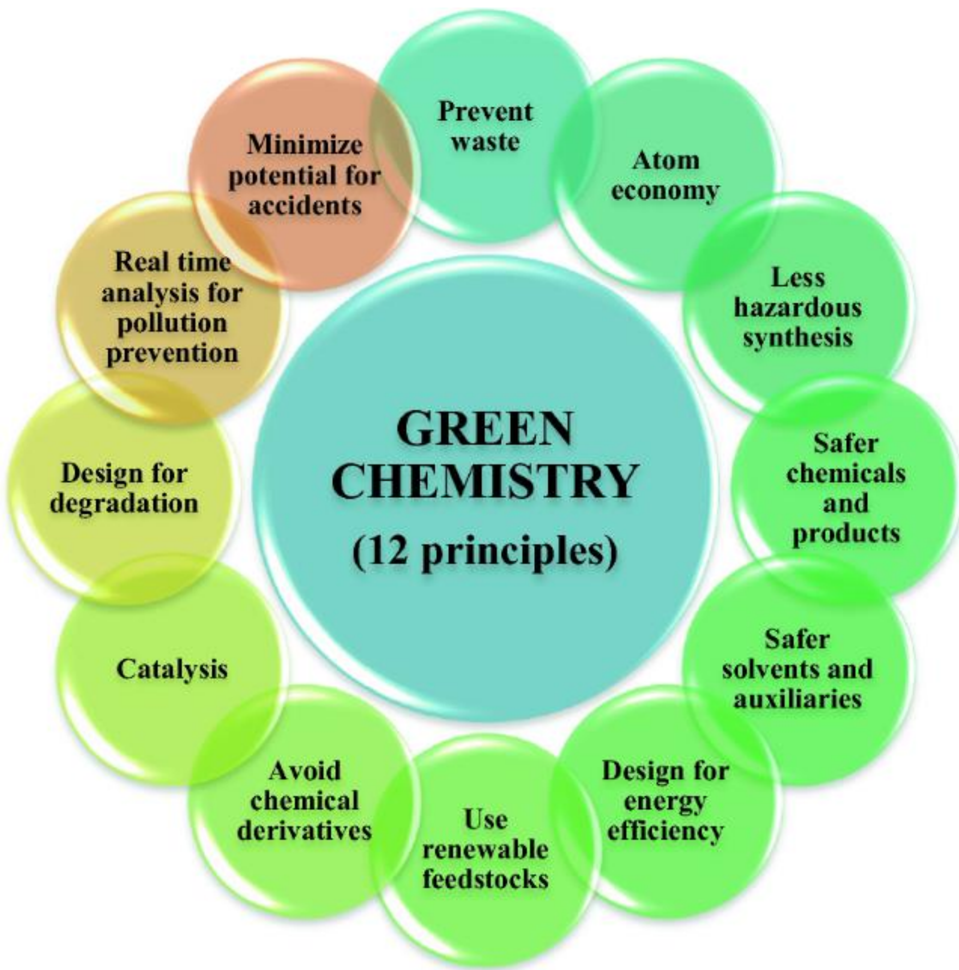
1. To reduce adverse environmental impact, try appropriate and innovative choice of material & their chemical transformation.
2. To develop processes based on renewable rather than non-renewable raw materials.
3. To develop processes that are less prone to objectionable chemical release, fires and explosion.
4. To minimize by-products in chemical transformation by redesign of reactions and reaction sequences.
5. To develop products that are less toxic.
6. To develop products that degrade more rapidly in the environment than the current products.
7. To reduce the requirements for hazardous persistent solvents & extractants in chemical processes.
8. To improve energy efficiency by developing low temperature & low pressure processes using new catalysts.
9. To develop efficient & reliable methods to monitor the processes for better and improved controls.

Green chemistry NOT a solution to all environmental problems BUT the most fundamental approach to prevent pollution.

Why do we need Green Chemistry?

Objective	Result
• Chemistry is undeniably a very prominent part of our daily lives. • Chemical developments also bring new environmental problems and harmful unexpected side effects, which result in the need for 'greener' chemical products.	• A famous example is the pesticide DDT.

❖ 12 Principles of Green Chemistry:



1. Prevention of Waste or by-products:

It is better to prevent waste than to treat or clean up waste after it is formed.

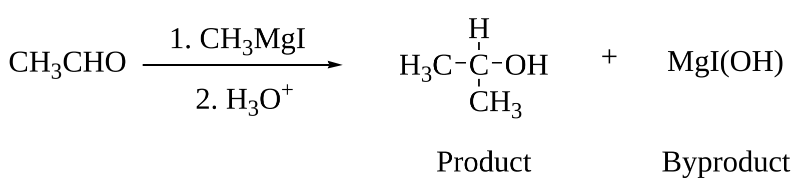
Any synthesis should be designed and carried out in such a way so that the waste or byproduct formation is minimum. It is however best if the byproducts or wastes are not generated. Also the overall cost of production is much more if the cost of treatment and disposal of waste is added to the overall cost. Waste is also obtained in case the starting materials and reagents are not fully utilized. The unreacted starting materials may or may not be hazardous.

2. Atom Economy:

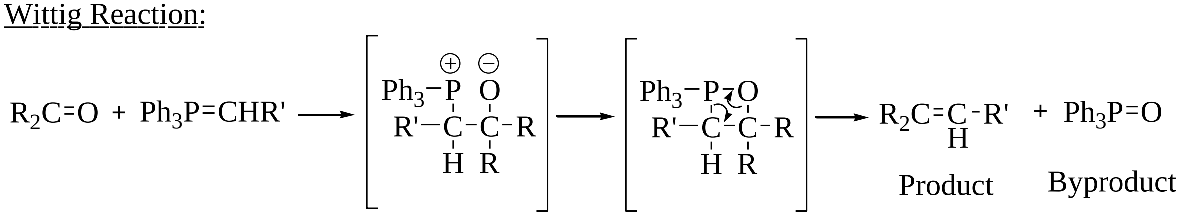
Synthetic methods should be designed to maximize the incorporation of all the starting materials in the process into the final product.

Normally if one mole starting material gives one mole product, the yield is 100%. Such reaction may generate byproducts or waste which is not visible. These reactions are not considered to be a green synthesis. E.g. Grignard reaction, Wittig reaction etc.

Grignard Reaction:



Wittig Reaction:



Atom economy (atom efficiency) describes the conversion efficiency of a chemical process in terms of all atoms involved (desired product produced).

$$\%\ \textit{Atom Economy} = \frac{\textit{Mol. weight of desired product}}{\textit{Mol. weight of all reactants}} \times 100$$

1. **Addition Reaction:** In this reaction all the atoms of starting materials are incorporated into the final product. So the reaction is 100% atom economical reaction.

$$H_3CH_2CHC{=}CH_2 \quad + \quad Br_2 \xrightarrow{CCl_4} CH_3CH_2CHBrCH_2Br$$

but-1-ene — 1,2-dibromobutane

Mol. wt. 56.06 — Mol. wt. 157.84 — Mol. wt. 213.90

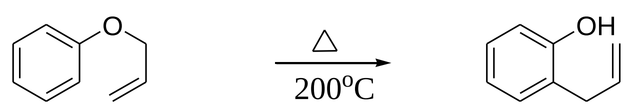
Deals Alder Reaction: Cycloaddition reaction of butadiene and ethyne gives 100% atom efficiency.

buta-1,3-diene — ethyne — cyclohexa-1,4-diene

Mol. wt. 54.05 — Mol. wt. 26.02 — Mol. wt. 80.07

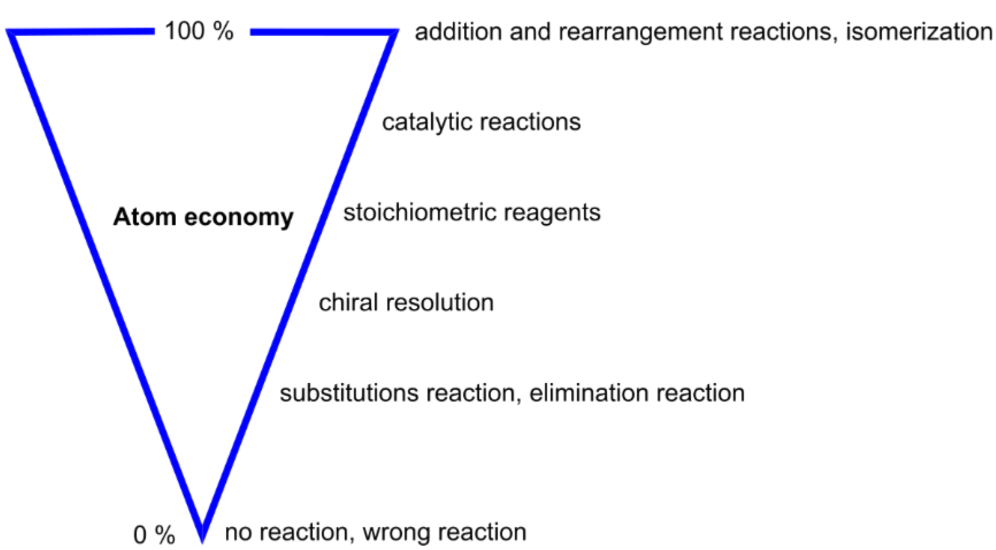
2. **Rearrangement Reaction:** These reactions involve rearrangement of atoms that form molecules. Hence atom economy of these reactions are 100%.

Claisen rearrangement:



Allyl phenylether — *o*-Allylphenol

Mol. wt. 134.07 — Mol. wt. 134.07



3. Minimization of Hazardous products:

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and environment.

In the context of green chemistry, not to use any hazardous starting material. It is equally important to make sure that no hazardous byproducts are generated in any synthetic procedure.

Example:

1. Avoid the synthesis of chemicals like organ mercurial compounds which caused minamata disaster.
2. Avoid the synthesis of methyl isocyanate (MIC) which caused Bhopal gas tragedy.

4. Designing Safer chemicals:

Chemical products should be designed to preserve efficacy of function while minimizing their toxicity.

The chemicals synthesized should not only be safe to handle but also should not have toxic effects. It is now possible to design safer chemicals due to development and advancement of technology.

Example:

1. Safer dry cleaning: Initially gasoline and kerosene were used, but now chlorinated solvents are used.
2. Supercritical or liquid carbon dioxide (CO_2)
3. Lead pollution has been decreased by replacing tetraethyl lead with less toxic additives (e.g. lead free gasoline) such as ETBE (ethyl tertiary butyl ether).

5. Safer solvents and auxiliaries:

The use of auxiliary substances (solvents, separating agents, extracting agents, etc.) should be non-toxic, non-explosive, non-hazardous, non-cancer causing, non-bio accumulated and non-mutation.

Example:

1. Water should be used as a solvent.
2. If water is not suitable then more ecofriendly solvents like super critical carbon dioxide or ionic solvents should be used as these are better solvents because they are non-toxic and non-explosive fluid.

3. As far as possible synthesis is carried out without solvents.

6. Design for Energy Efficiency:

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized.

It is necessary to design the chemical processes or products in such a way that it utilizes less energy to form desired product, this can accompany by keeping the chemical processes at ambient temperature and pressure in the presence of suitable catalyst.

- This can be achieved by:
  - Synthetic methods should be conducted at ambient temperature and pressure.
  - Developing the alternatives for energy generation such as photovoltaic, hydrogen, fuel cells, bio based fuels etc.
  - Use of microorganisms for organic synthesis.
  - Use of proper catalyst, enzyme.
  - Use of renewable materials.

Example:

Formation of ammonia by Haber's process

$N_2 + 3H_2 \longrightarrow 2NH_3$

Temperature= 673-723 K, Pressure= 200 atm, Catalyst= Iron

7. Use of Renewable feedstock:

A raw material or feed stock should be renewable rather than depleting whenever technically and economically practical.

For sustainable development, it is better to avoid exploitation of non-renewable natural resources like petroleum, coal and natural gas etc. But use of renewable resources for its sustainable development did not create much problem because it is restored by natural processes and biogeochemical cycle.

Example:

An example of renewable starting materials are agricultural products i.e. formation of furfural from bagasse and waste biomass of wheat and rice plant etc.

8. Reduce Chemical Derivatives:

Unnecessary derivation such as use of blocking group, protection and deprotection, temporary modification of physical or chemical processes should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

More derivatives involve:

- Additional reagents
- Generate more waste products
- More time
- Higher cost of products. Hence, it requires to reduce derivatives.

Example:

Use of enzymes to avoid protecting groups and cleanup process is the industrial synthesis of semi synthetic antibiotics such as ampicillin and amoxicillin.

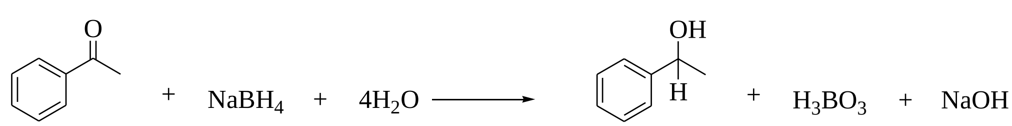
9. Catalysis:

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Catalyst is the chemical substance which is used in small quantities, enhance the rate of reaction by decreasing activation energy and regenerate itself at the end of reaction. But the stoichiometric reagent is used in large quantity and does not generate at the end of reaction. Different types of catalysts are available including phase transfer catalysts, biocatalysts, etc.

- Catalysts make the
  - reaction faster
  - decrease the energy requirement
  - can produce single desired product
  - minimize waste

Example:



Atom Economy = 81%

Atom Economy = 100%

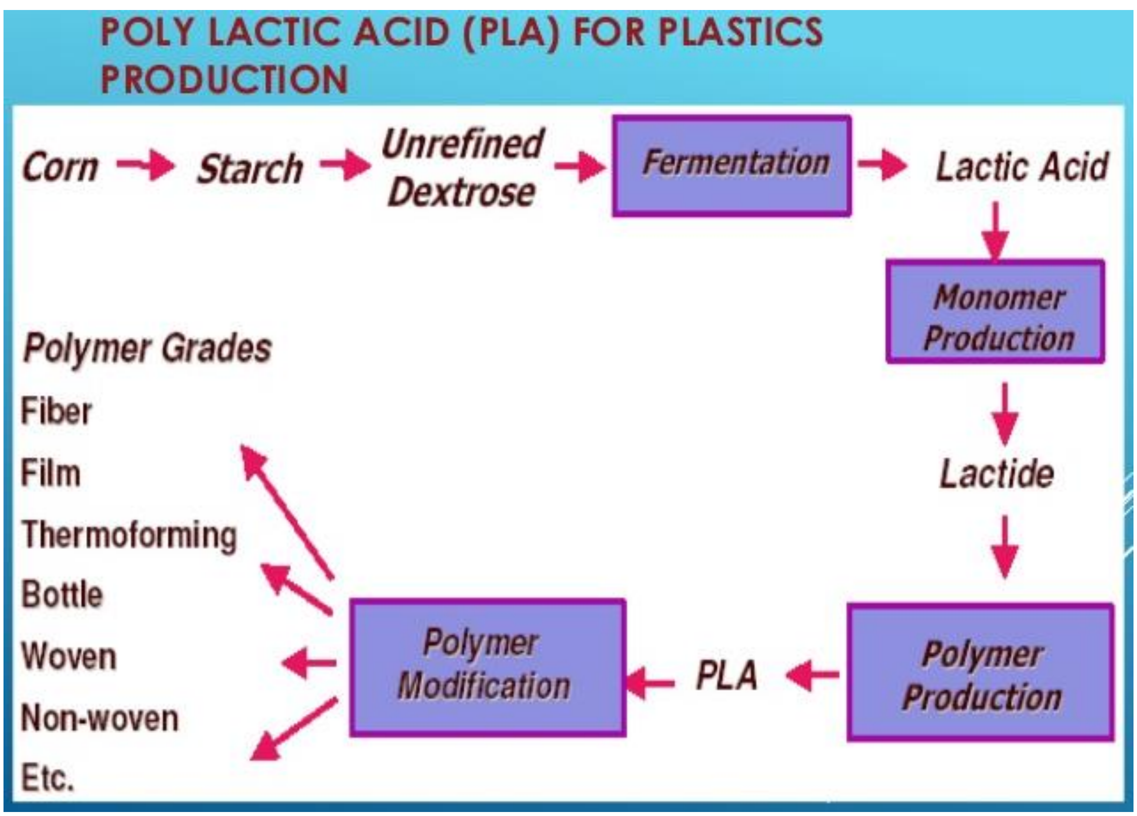
10. Design for degradation:

Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

- The chemical processes and products should be design in a way that the desired products and waste products formed by the process are biodegradable in natural environment.
- The desired products are break down into harmless small substances by physical, chemical and biological means and do not persist in the natural environment.
- The products should not be bio accumulative in nature and do not show bio magnifications.

Example:

1. Synthetic insecticides remain in the food grains and vegetables and do not get degraded but natural insecticides (chilli, neem etc.) get easily degraded after killing the insects.
2. Biodegradable and bioactive thermoplastic aliphatic polyester polylactic acid (PLA).



11. Real time analysis for pollution prevention:

Analytical methodologies need to be further developed to allow real-time, in process monitoring and control prior to the formation of hazardous substances.

It is important to know the event's or the products formation during a chemical process at different temperature, pressure and time to control the formation of desired products and to avoid formation of any hazardous substances or waste substances as byproduct.

12. Safer chemicals for accident prevention:

Substances and the form of substances used in chemical process should be chosen so as to minimize the potential for chemical accident, including releases, explosion and fires.

Design chemical processes and products and their physical states like solid, liquid and gaseous form to minimize or eliminate the potential of chemical accidents including explosion, fire and smoke produce due to chemical and release into the natural environment. The use of volatile organic solvents in chemical industries have also resulted in fires and explosions.

- Hazardous substances are:
  - Corrosive
  - Flammable
  - Explosive
  - Reactive
  - Toxic
- To prevent accidents and injuries the following right steps should be taken before handling any hazardous substances:
  - The reagents and reaction should be risk free in the chemical process to minimize the chemical accidents, explosion, fires and gas release.
  - Read labels and SDSs (Safety Data Sheets) to learn about hazardous and required safety precautions.
  - Check for adequate ventilation.
  - Remove items from the work area that could ignite or react with hazardous materials.
  - Know the location of fire extinguisher, emergency alarms, eyewash stations and first-aid kits.